

SULFUR DIOXIDE UTILIZATION BY THE TREATMENT OF PYRITE- CHALCOPYRITE SULFIDE CONCENTRATES, COMBINING MECHANICAL AND METALLOTHERMIC PROCESSES

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Abstract: *In the research a new non-conventional technology for the treatment of local pyrite-chalcopyrite sulfide concentrates is suggested allowing to extract copper and iron from the concentrates by an energy-saving, efficient and ecologically friendly method. For this purpose the reactivity of pyrite-chalcopyrite sulfide concentrates was enhanced for further intensification of metallurgical processes and obtaining of the copper-iron ligatures by direct aluminothermic reduction of activated concentrates.*

With the object of increasing the chemical activity of pyrite-chalcopyrite concentrates, they were subjected to preliminary mechanochemical activation in the vibratory mill. Fine grinding was carried out in air, water and applying other combined methods. In all cases mechanochemically activated copper and iron sulfides underwent deep chemical transformations forming metal sulfates, hydrosulfates, and partly oxides. Thus, mechanical activation of sulfides led to the same effect that takes place during the low-temperature roasting in the furnace.

Then the mechanochemically activated (MA) concentrate was reduced by aluminothermy. The combination of mechanochemistry with the metallothemy allowed to perform a unique reduction process with more efficiency, and to obtain modified copper-iron ligatures bypassing the roasting processes common for the traditional metallurgy that lead to formation of volatile sulfur oxides.

The structure of the obtained ligature was also examined. Metallographic analysis shows that it depends on the duration of mechanochemical activation. It is characterized by the microheterogeneous nature, is more dispersed and presents a mechanical mixture of iron and copper (47% Fe, 53% Cu).

Keywords: *mechanochemical, copper concentrate, iron concentrate, sulfate, grinding, planetary mill, aluminothermic reduction.*

1. Introduction

In the area of industrial progress of the Republic of Armenia the issues of developing materials with required properties and advanced technologies for their production are of special interest. Particularly, great attention has attracted to alloys with new structures, that exhibit high strength, durability and corrosion resistance in different aggressive media.

Among these alloys are iron bronzes, which are doped by copper-iron ligatures. The production of such ligatures by traditional methods is a complex and energy-consuming process that requires expensive equipments. Taking into account the demand for iron bronzes and high content of copper in concentrates obtained in RA, it is advisable to organize such local production. For this production Kapan pyrite-chalcopyrite sulfide

concentrate with the copper content from 18 to 20% may be used as a raw material. These concentrates currently are exported, while organization of the local production for complex and ultimate processing of raw materials would provide the most economical benefits. On the other hand, copper production by the traditional technology is a complex process requiring expensive equipments and is associated with some difficulties. So far the problems related to the recycling of SO₂ and iron extraction from final tailings (with iron content up to 38%) remain insoluble. From this point of view it is vital to develop new alternative technologies for

2. Experimental

Investigations were carried out on the copper concentrate from Kapan (in south of Armenia) deposit. Average chemical composition of the concentrate is as follows: Cu-27.2%; Fe-24.1%; S-29.1%; Σ80.4%, the rest are SiO₂ and non-mineral materials.

Mineralogically, Kapan deposit's composition is as follows: chalcopyrite (CuFeS₂) – 60%; chalcocite (Cu₂S) – 8%; pyrite (FeS₂) – 5%; tenorite (CuO) – 4%; bornite (Cu₅FeS₄) – 3%. As it could be seen, the concentrate mainly is composed of pyrite and chalcopyrite, that's why they are called of the pyrite-chalcopyrite type. Pyrite occurs in free form.

Vibration planetary mill (2474 rpm) was used for grinding (pretreatment) of the chalcopyrite concentrate (down to -0.1 + 0.74 mm in size). Around 50 g sample was thus vibro-treated. Mill ball diameter is 0.8

3. Results and Discussion

X-Ray diffraction patterns of initial concentrate as well as the pretreated

the pyrite-chalcopyrite sulfide concentrates, which will make possible to extract with minimal economic costs not only copper, but also iron up to the metallic state in the form of ligatures, bypassing the roasting process. Thereby, it is of prime interest to develop a new approach for metallothermic reduction of sulfide concentrates combined with the preliminary mechanochemical activation, which promotes of obtaining fundamentally new modified products. Based on the foregoing, the development of a modern technology of obtaining copper-iron ligatures from the pyrite-

cm, weight: 1750 gr. Both dry and wet (in aqueous media) grinding was used. solid to liquid (S:L) ratio was at 1:1.5 for wet grinding, duration: 30, 60, 90, 120 min.

The sample obtained after the experiments was filtered for the quantitative determination of copper and iron in the solution, both by the atomic-adsorption and photo-calorimetric methods. X-ray diffraction (XRD) examination with monochromatic λCuKα radiation (DRON-2 diffractometer) was performed. Scanning electron microscope (SEM) VEGA TS 5130MM, Tescan, Czech Republic, Microanalysis System INCA Energy 300, Oxford Instruments, UK7 and Energy Dispersive X-ray microanalyzer were used for metallographic investigations. In addition, current inspections of initial mixtures and final products were realized by a "Neophot-32" microscope (Germany).

samples (dry and wet activated) are presented in Fig. 1.

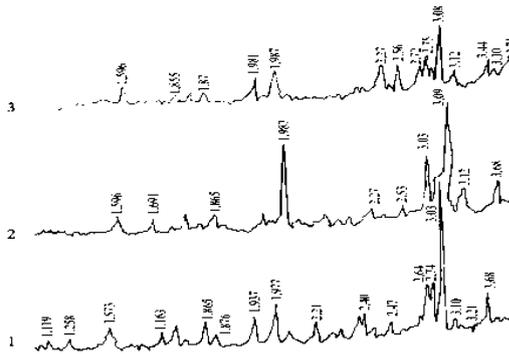


Fig. 1. Diffraction patterns of the copper concentrate from Kapan deposit
1- initial concentrate; 2- dry activated; 3- wet activated. Duration: 1 h.

As it follows from the figure (Fig. 1, curve 1), there are strong reflexes pertaining to 3.12, 3.03, 1.85 Å, which are characteristic of chalcopyrite. One could discern also reflexes of pyrite: $d=3.14, 2.71, 2.21, 1.637$ Å. Chalcozin-characteristic reflexes are: $d=3.39, 2.40, 1.969, 1.87, 1.695$ Å, while the 2.72, 1.937, 1.876, 1.258 Å reflexes pertain to bornite.

3.31, 3.10 Å patterns of the initials are also present in the X-Ray plots, the quantity of which, according to their intensities, are not high. The basic lines coincide with standards.

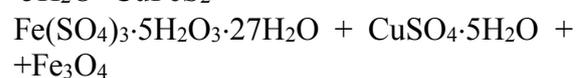
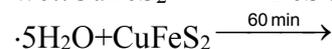
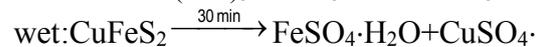
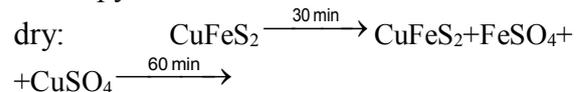
Thus, the X-Ray and the mineralogical data coincide.

Pyrite-chalcopyrite concentrate's characteristics undergo steep changes after the mechanical treatment. New reflexes are appeared after dry mechanical treatment, 1 h. The lines: $d=2.53; 1.596, 1.696$ Å are characteristic of magnetite; the lines: $d=4.85, 3.44, 3.12, 2.52$ Å are characteristic of $FeSO_4$; and 5.11, 3.68, 3.13, 3.09, 2.84, 1.985, 1.897 Å are characteristic of $Fe_2(SO_4)_2$. For some cases, these reflexes coincide with iron oxide reflexes.

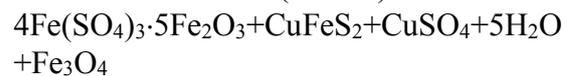
Wet treatment produces reflexes which are characteristic of sulphate crystal-hydrates: $4Fe_2(SO_4)_3 \cdot 5Fe_2O_3 \cdot 27H_2O$, ($d=5.11, 3.13, 3.09, 2.55, 1.987, 1.838$ Å); $FeSO_4 \cdot H_2O$ ($d=3.99, 3.44, 3.12$ Å) and $CuSO_4 \cdot 5H_2O$ ($d=5.48, 4.73, 3.99, 3.71, 2.75$ Å):

On the other hand, characteristic lines of chalcopyrite and of other minerals gradually tend to decrease. The intensity of characteristic line's at 3.03 Å is reduced turning primarily into $d=3.08$ Å, which is characteristic of $Fe_2(SO_4)_3$. SO_4^{2-} ions are present in the activated samples in considerable quantities (SO_4^{2-} ions were determined by $BaCl_2$).

Here are some phase transitions of chalcopyrite due to mechanical activation:



combined treatment (60 min):



During wet activation in water, the structures of chalcopyrite and chalcocite are disintegrated, as follows from intensity reduction of $d=1.870$ and 1.855 Å lines characteristic of $CuFeS_2$. New phase is emerged: $4Fe(SO_4)_3 \cdot 5Fe_2O_3 \cdot 27H_2O$, along with $CuSO_4 \cdot 5H_2O$ phase being present in considerable quantities. This new phase is a result of consistent crystallization (the sharp peaks at $d=3.12$ and 5.08 Å lines). Hence, effective activation already holds right in the initial phase of activation. Further grinding makes $4Fe(SO_4)_3 \cdot 5Fe_2O_3 \cdot 27H_2O$ phase more crystalline, which is confirmed by the sharp reflex of 3.08 as well as 4.73 line being characteristic of $CuSO_4 \cdot 5H_2O$.

The interstitial plane distances of $4Fe_2SO_4 \cdot 5Fe_2O_3 \cdot 2H_2O$ and chalcopyrite are the same equaling to 3.08 Å. Actually, $CuFeS_2$ is transformed into $Cu_9Fe_9S_{16}$. Thus, chalcopyrite losses most of the sulphur during mechanical treatment.

From above said it follows that dry and wet activation (1 h) causes mechanical-

chemical changes, and chalcopyrite-pyrite concentrate diffraction pattern undergoes deep changes. Chalcopyrite crystal structure becomes amorphous after dry grinding which later re-crystallizes in hexagonal trigonal lattice structure of the following: CuFeS_2 (2.04 Å), up to oxidized: CuSO_4 , FeSO_4 , $\alpha\text{Fe}_2\text{O}_3$ (2.68 Å) and Fe_3O_4 (2.74, 2.53, 1.691):

Thus, mechanochemical activation experiments showed that preliminary mechanochemical activation process in the vibratory mill of Kapan (Armenia) pyrite-chalcopyrite sulfide concentrates is similar to the low-temperature roasting of minerals. In both cases the process is accompanied by the transformation of sulfides into sulfates, hydrosulfates and oxides. Investigations have been carried out aimed at direct, out-of-furnace aluminothermic reduction of previously mechanochemically activated concentrates. Preliminary thermodynamic calculations showed that aluminothermic reduction of iron and copper sulfates are possible, and these reactions are characterized by high thermal effect and by negative values of ΔG .

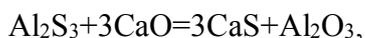


$$\Delta G = -4431.76 + 2.72T \text{ kJ/mol}$$



$$\Delta G = -4894.34 - 0.36T \text{ kJ/mol}$$

Most probably the following reaction takes place as well:



$$\Delta G = -693.86 - 0.59T \text{ kJ/mol}$$

Therefore, one can assume that due to the mechanochemical activation, the transformation of sulfides into sulfates promotes their aluminothermic reduction and extraction of sulfur in the form of CaS. Aluminothermic reduction was carried out with the samples prepared from the mixture of copper concentrate, aluminum powder, copper shavings, CaO and NaNO_3 [7,8]. As a result metallic and slag phases were obtained, which were easily separated from each other after the

cooling. The dependence of the extraction degree of the metallic phase from the amount of reducer was studied at fixed content of other components and at various milling durations. It has been found that the degree of metallic phase extraction strongly depends on the particle size of the reducer and its quantity. In the case of 60 minutes of milling duration and theoretically necessary amount of the reducer, the reduction proceeds with low efficiency and partly separation between the metal and slag phases takes place. Besides, the metallic phase contains sulfur traces. At the same milling conditions and at 120% excess of the aluminum in the initial mixture the reduction proceed violently resulting in formation of a metallic phase where traces of sulfur were also detected. In all cases the metallic phase (with the yield of 81%) represented a mixture of iron and copper. This alloy was porous because of significant sulfur content. To increase the yield of the metallic phase by the increasing of aluminum amount in the initial mixture is not reasonable, because this leads to an increase of the aluminum content in the final product (up to 1.0-1.5%) and the specific heat of the process as well. To decrease the specific heat of the reaction and to avoid the presence of sulfur in the alloy, the dependence of the metallic phase extraction degree from the amount of the fusible additive, CaO, was studied at the same composition of initial mixture and 60 minutes milling duration. The best results were obtained at 30% content of CaO. In this case the metallic phase and the slag were separated easily, resulting in growth of the alloy yield up to 90-92% and low sulfur content (0.01%). Thus, the addition of quicklime promotes the transition of sulfur into the slag. The dependence of the extraction degree of the metal phase from the content of NaNO_3 was also studied. As a result the following improved optimum composition of the initial mixture was

established: copper concentrate - 50%, aluminum powder - 13%, NaNO_3 - 5%, copper shavings - 2%, CaO - 30%. At this composition and 90 minutes of milling duration the extraction degree for the ligature reaches about 98.9% with low content of sulfur (0.01%). The metallic phase obtained was subjected to chemical analysis, resulting in copper and iron contents of 53% and 47%, respectively, without traces of sulfur and aluminum. Metallographic analysis has shown that increase in the milling degree does not change chemical composition of the alloy, while an influence on the structure and particle size distribution is significantly higher.

As it follows from the structure of non-activated samples (Fig. 2.1) the metallic phase is distributed irregularly in the form

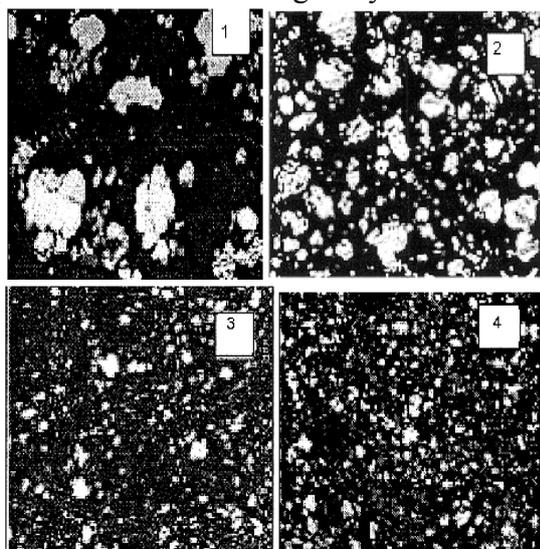


Fig. 2. Microstructures of the metallic phases obtained at different milling conditions and non-activated initial mixture (x 400): non-activated (1), samples activated for 15 min (2), 30 min (3) and 60 min (4).

of agglomerations. The microstructure of the metallic phase obtained after 15 min activation (Fig. 2.2) differs significantly. Here metal particles are larger hypothetically as a result of agglomeration caused by strong surface forces. Activation during 30 minutes (Fig. 2.3) allows to obtain metal particles with a smaller size

and more uniform distribution, and 60 minutes activation leads to the formation of a more fine-grained microheterogeneous structure (Fig. 2.4).

Thus, comprehensive studies prove the fundamental possibilities of producing the copper-iron ligatures by the direct aluminothermic or silicothermic reduction of mechanochemically activated copper sulfide concentrates. The modified alloy obtained by such a method can be used as alloying agent in the production of different copper alloys and bronzes.

4. Conclusion

The behavior of Kapan copper concentrate was investigated during fine grinding in the vibratory mill in water or in air for durations of 15, 30 and 60 minutes. It was shown that both the separate minerals and the copper concentrate undergo deep chemical changes in these environments during fine grinding. In addition, milling in the air for 60 minutes leads to the formation of copper and iron sulfates, and iron oxides (Fe_2O_3 and Fe_3O_4) in the case of iron. Hydrosulfates were obtained in water environment at the milling duration of 60 minutes. It was shown that the formation of sulfates and oxides during the mechanochemical activation partly replaces the roasting process, making the further reduction process of sulfides more vigorous.

Technical parameters were selected for the aluminothermic reduction of copper concentrate and structure investigations of the obtained alloys were carried out. Metallographic analysis has shown that the structure of depending on the activation duration a more dispersed and microheterogeneous alloy is obtained.

A technology was developed for the production of copper-iron ligatures by a direct out-of-furnace aluminothermic reduction of the Kapan copper concentrate. This energy-saving technology helps also

to solve some environmental issues, including the extraction of SO₂ and can be easily applied in factories operating in Yerevan, where ferroalloys are producing by similar technologies.

6. References

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